

Thermal conductivity of maleated polyethylene/layered silicate nanocomposite

Sang Hyun Lee¹, Jeong Eun Kim², Hyun Hoon Song² and Sok Won Kim³

1 Division of Physical Metrology, Korea Research Institute Standards and Science, Daejeon 305-600, Korea.

2 Dartment of Polymer Science and Engineering, Hannam University, Daejeon 306-700, Korea.

3 Department of Physics, University of Ulsan, Ulsan 680-749, Korea.

ABSTRACT

Nanocomposites are a new class of composites in which the reinforcing phase dimensions are in the order of nanometer scale. In particular, the layered silicates are considered to be good candidates for the preparation of polymer-inorganic nanocomposites. The mechanical and thermal properties of polymer can be altered by adding a few vol % of the nano-particles.

In this study, we focused on the effect of the nano-sized particles on thermophysical properties such as melting and crystallization, coefficient of thermal expansion, and thermal conductivity. We prepared the PEMA/layered silicate nanocomposites and the thermophysical properties were investigated by DSC and 3ω method. The content of layered silicate was varied from 0.5 vol.% to 5 vol.%.

KEY WORDS: PEMA/silicate nanocomposite, melting and crystallization, thermal conductivity, thermal expansion, three omega

1. INTRODUCTION

One of the most promising composites is a hybrid system consist in organic polymers and inorganic materials including layered silicates. [1-9]. In particular, the layered silicates are considered to be a good candidate for the preparation of organic-inorganic nanocomposites. The nanocomposites are a new class of composites in which the reinforcing phase dimensions are in the order of nanometers. The silicate layer content in the nanocomposite is only a few volume fraction, which is about one-tenth of the reinforcing filler content in conventional polymer based composites. But, still the mechanical and thermal properties of polymer/silicate nanocomposites are far superior to those of conventional composites[10]. In recent years, the invesigation of polymer/clay nanocomposite has become a very important research field[11]. Melt intercalation of polymer matrix into the layered silicate is the most typical method to prepare the polymer/silicate nanocomposites and many kinds of polymer matrices were examined such as PS[12,13], PP[14,15], PE[16,17], polyimide[4], etc.

Among many physical and chemical properties of the nanocomposties, thermal properties, especially, thermal stability, thermal conductivity, and thermal expansion are of our great interest. Thermal expansion behavior of nylon 6 nanocomposites was investigated [18]. The thermal expansion was highly affected by the alignment of exfoliated platelets. Small changes from perfect planar orientation result in significant changes in thermal expansion behavior. In polyurethane/layered silicate nanocompostie, the thermal conductivity was slightly decreased with the increase of silica content[3]. However, by a small amount of clay, the coefficient of thermal expansion was decreased about 45%, which was ascribed to the high aspect ratio of the exfoliated silicate layers[19]. The maleated polyethylene (PEMA)/silicate nanocomposite was also studied in regard to the behavior of melting and crystallization, morphology, and mechanical properties[20]. The crystallization and melting temperatures of the nanocomposites were strongly related to the filler content and its dispersion state.

In this work, the thermophysical properties such as melting and crystallization, thermal expansion coefficient, and thermal conductivity of PEMA(maleic anhydride modified polyethylene)/layered silicate nanocomposite were investigated by DSC, TMA, and 3ω method, respectively. The silicate content was varied from 0.5 vol % to 5 vol %.

2. SAMPLE PREPARATION

Maleic anhydride(MA) was used as the modifier of polyethylene(PE). Maleic anhydride modified polyethylene(PEMA) was 0.85 wt% maleic anhydride grafted for matrix materials and purchased from Aldrich. The organic filler was used to the

SiO₂(synthetic silica) from Fuji Sylsya(synthetic silica, Sylsya 350). The average particle size of these silica is about 1.8 μ m. The polyethylene/silicate nanocomposite prepared by melt intercalation at 140 °C using a brabender mixer with the screw speed of 60 rpm and the mixing time was 15 minutes. The silica filler contents were prepared from 0.5 to 5 vol% in nanocomposites.

Fig. 1 shows the conceptual approach to the monomer intercalation. Intercalated structure in which a single, and sometimes more than one, extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in continuous polymer matrix, an exfoliated or delaminated structure is obtained[1].

3. EXPERIMENTAL

The thermal behaviors of PEMA/silicate nanocomposites were investigated by means of DSC (differential scanning calorimetry; Perkin-Elmer Pyris-1 differential scanning calorimeter with samples weights of 5 ~ 10 mg). All operations were carried out under a nitrogen environment with a flow rate of 30 ~ 50 mL/min and a heating rate of 10 K/min. Before the thermal analysis, the samples were heated to 160 °C to eliminate the influence of thermal history. The polymer crystallinity can be determined with DSC by quantifying the heat of fusion of polymer[21]. In the case of polyethylene, DSC can be used to measure the degree of crystallinity by rationing the heat of fusion for a specific sample versus that for a 100% crystalline standard. DSC was calibrated by indium and zinc pure materials for temperature and heat of fusion.

The thermal expansion coefficient was measured by TMA (thermomechanical analyzer; Setaram TMA92) under an argon gas atmosphere. Rectangular samples (5 mm x 5 mm) were prepared and dried in an oven at 105 °C for 2 hours to remove moisture. The thermal expansion tests were performed in the temperature range from 20 to 80 °C at a rate of 5 K/min. The data of thermal expansion were averaged for 4 measurement runs of 2 samples.

The thermal conductivity was measured by the 3 ω method. The 3 ω method has been widely utilized for the thermal conductivity measurement of bulk and film type samples. An ac current at frequency ω heats the sample and this signal includes thermal information[22,23]. The schematic diagram of our apparatus is depicted in Fig. 2. The heater and thermometer is used to the metals. The metal strip line heater made of gold is about 20 μ m wide and 3 mm long. Thin gold films were evaporated on sample by

thermal evaporator. The electrical resistance of gold layer was controlled about 10 Ω ~ 30 Ω by controlling the evaporation time . The metal strip line is functioning as both the heater and the thermometer for detecting 3 ω signal.

The thermal conductivity of 3 ω apparatus was calculated from [23]

$$\lambda = -\frac{V^3}{4\pi l R^2} \frac{dR}{dT} \frac{d \ln \omega}{dV_{3\omega}'}$$

where $V_{3\omega}'$ is the in-phase 3 ω voltage at frequency ω . TCR(temperature coefficient of resistance) is defined as $\frac{1}{R} \frac{dR}{dT}$. R is the average resistance of the heater/thermometer

line, V the voltage across the metal line at ω , and $V_{3\omega}$ the measured voltage at 3 ω .

TCR was measured by a four-probe method prior to 3 ω measurements. As illustrated in Fig. 2, the experimental apparatus of 3 ω system consists of a function generator for ω signal, differential amplifier for signal detection, and lock-in amplifier for 3 ω signal.

4. RESULTS AND DISCUSSION

Figure 3, 4 shows a DSC melting and crystallization curve of the PEMA and PEMA/silicate nanocomposites. Thermal properties of the PEMA and PEMA/silicate nanocomposites are shown in Table I. The PEMA shows an onset temperature at 118.5 $^{\circ}\text{C}$ and a peak temperature 124 $^{\circ}\text{C}$. The onset and peak temperature was decreased with the increase of silicate filler content. The melting or crystallization of PEMA/nanocomposites shows a broad temperature range, so we analyzed the data from 60 to 130 $^{\circ}\text{C}$ region. It's apparent that the onset temperature and the peak center decrease with the silicate filler content, even though the amount of change is only minimal.. The PEMA/silicate nanocomposites also show double peak on melting and crystallization when SiO_2 content is higher than 3 vol %. The % crystallinity of the nanocomposites was estimated in reference to 290 J/g for a 100% crystalline polyethylene[21]. The crystallinity of PEMA/silicate nanocomposite were 19.7% ~ 27.0% and the crystallinity decreased linearly with the contents of silicate volume fraction. These results are very similar to those (35%~39%) obtained from XRD peak profile[23]. The crystallinity of the PEMA/silicate nanocomposites from DSC measurement are shown in Fig. 5.

Thermal expansion rate of PEMA/silicate nanocomposites are shown in Fig. 6. This value was calculated by rating of elongation length/initial length(L/L_0*100). The thermal expansion rate increased with the temperature increase. The rate of thermal expansion appears to remain constant with the silicate content from 0.5 to 3vol% silicate, but that of 5vol% clearly decreased to a value lower than that of PEMA. The coefficient

of thermal expansion (CTE) of PEMA at room temperature was $16.11 \times 10^{-5}/\text{K}$, which well agrees with reported data of CTE of PE, $10 \times 10^{-5}/\text{K} \sim 22 \times 10^{-5}/\text{K}$ [24]. The CTE of nanocomposite at 30 °C is $10.59 \times 10^{-5}/\text{K}$, $10.02 \times 10^{-5}/\text{K}$, $11.16 \times 10^{-5}/\text{K}$, $4.99 \times 10^{-5}/\text{K}$ for 0.5vol%, 1.0vol%, 3.0vol%, 5vol%, respectively. The thermal expansion of the pure PEMA at 80 °C is almost 3 times as large as that of PEMA/silicate of 5vol%. As the amount of silicate increases, the thermal expansion rate decreases. The effective reduction in thermal expansion for the nanocomposites is believed to stem from the nature of the filler, e.g. high modulus, high aspect ratio, two-dimensional reinforcement, and low CTE [18].

Thermal conductivity of the PEMA and PEMA/silicate nanocomposites are shown in Table II and Fig. 7. The thermal conductivity of PEMA at 300 K was 0.61 W/(mK). This value is slightly higher than the reference value of PE that is 0.3 ~ 0.53 W/(mK) [24]. In general, most polymers show thermal conductivity ranging from 0.1 to 0.6 W/(mK) and the thermal conductivity of polymers filled with inorganic fillers shows increment. With the increase of temperature, thermal conductivity for crystalline polymers decreases gradually below the melting temperature. But amorphous polymers, the thermal conductivity increases slowly with the increase in temperature below the glassy region. Fig. 7 shows that the thermal conductivity of nanocomposite decreases linearly with temperature. The thermal conductivity of SiO_2 is 1.37 W/(mK) [23] which is higher than that of PEMA. Therefore, the addition of organic filler should raise their thermal conductivities with the increase of loading volume. The thermal conduction of polymer may be affected by the density, orientation of chain segments, etc. But these nanocomposites, as revealed by TEM and SEM study, exhibit very poor dispersion of silicate filler and also irregular size distribution of silicate particles indicating aggregation [20]. Our unusual thermal conduction was probably affected by the poor dispersion of SiO_2 particles. We estimated our apparatus uncertainty level is about 5%, but the uncertainty of 3 ω method was found to be larger. The round robin test by VAMAS to measure the thermal conductivity by 3 ω method of silicon dioxide films was scattered about $\pm 25\%$ [25]. On the other hand, the thermal conductivity of polyurethane/layered clay nanocomposite decreased slightly with increasing weight fraction of layered clay [3], which is similar to our results. Fig. 8 shows the relation between thermal conductivity and the volume fraction of silicate filler at 300 K. These data of nanocomposites were scattered about $\pm 8.6\%$. By increasing the volume fraction of layered silicate, the thermal conductivity decreased slowly rather than increased.

5. CONCLUSIONS

Thermophysical properties of PEMA/silicates nanocomposites, including melting and crystallization, thermal conductivity, and coefficient of thermal expansion, were investigated by DSC, TMA and 3ω method. The onset and peak temperature was decreased with the increase of silicate filler content. The onset temperature decreased about 7~9 °C. The crystallinity of PEMA/silicate nanocomposite linearly decreased with the contents of silicate volume fraction. The rate of thermal expansion was not affected by the silicate content from 0.5 to 3vol%, but shows clear decrease to a value lower than that of PEMA when the content is 5vol %. The thermal conductivity of nanocomposite rather decreased linearly with the temperature increase. These results can be attributed to the poor dispersion and size distribution of silicate particles throughout the polymer matrix. It appears that the thermophysical properties of nanocomposites could be accurately characterized on the basis of detailed knowledge of structure and morphology .

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Table I. Thermal propertie of PEMA/SiO₂ composites.

Silicate volume fraction %	Onset temperature °C	Peak temperature °C	Heat of fusion J/g	Crystallinity %
0	118.5	124.0	114.4	41.1
0.5	111.6	118.2	77.6	27.0
1.0	111.0	118.1	76.2	25.4
3.0	109.4	118.1	69.7	23.9
5.0	109.7	117.4	57.4	19.7

Table II. Thermal Conductivities of PEMA/silicate nanocomposites.

Temperature K	$\lambda/W/(mK)$ PEMA	$\lambda/W/(mK)$ PEMA/lapo vol%		$\lambda/W/(mK)$ PEMA/SiO ₂ vol%			
		1%	3%	0.5%	1%	3%	5%
160	1.960	-	-	1.58	1.71	1.78	1.69
180	1.52	-	-	1.30	1.39	-	1.39
200	1.27	-	-	1.11	1.13	1.20	1.22
220	1.04	-	-	0.96	0.95	0.99	0.95
240	0.86	0.58	0.42	0.85	0.80	0.83	0.80
260	0.75	0.50	0.37	0.75	0.69	0.70	0.68
280	0.65	0.43	0.32	0.68	0.60	0.60	0.59
300	0.61	0.39	0.28	0.62	0.54	0.53	0.51

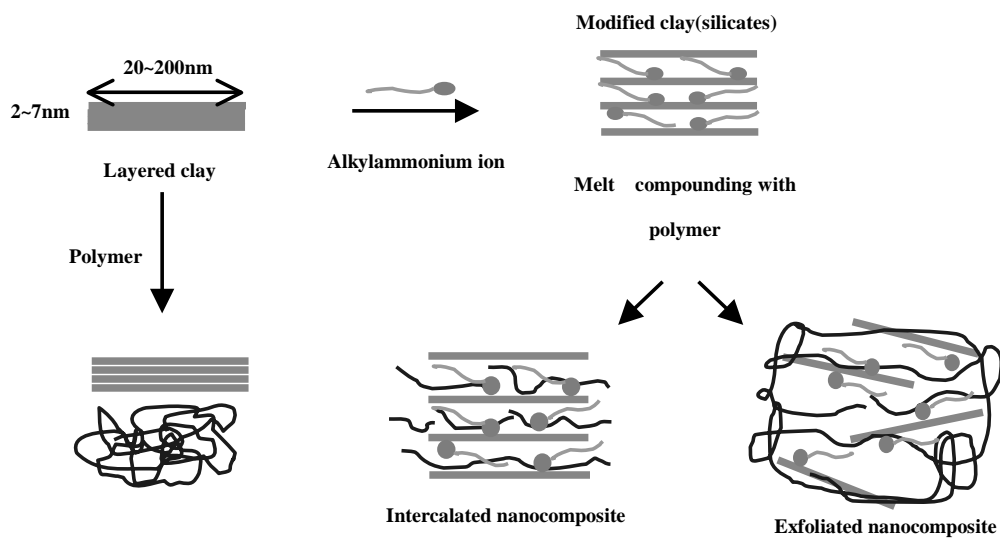


Fig. 1 Schematic representation of polymer/silicate nanocomposite preparation.

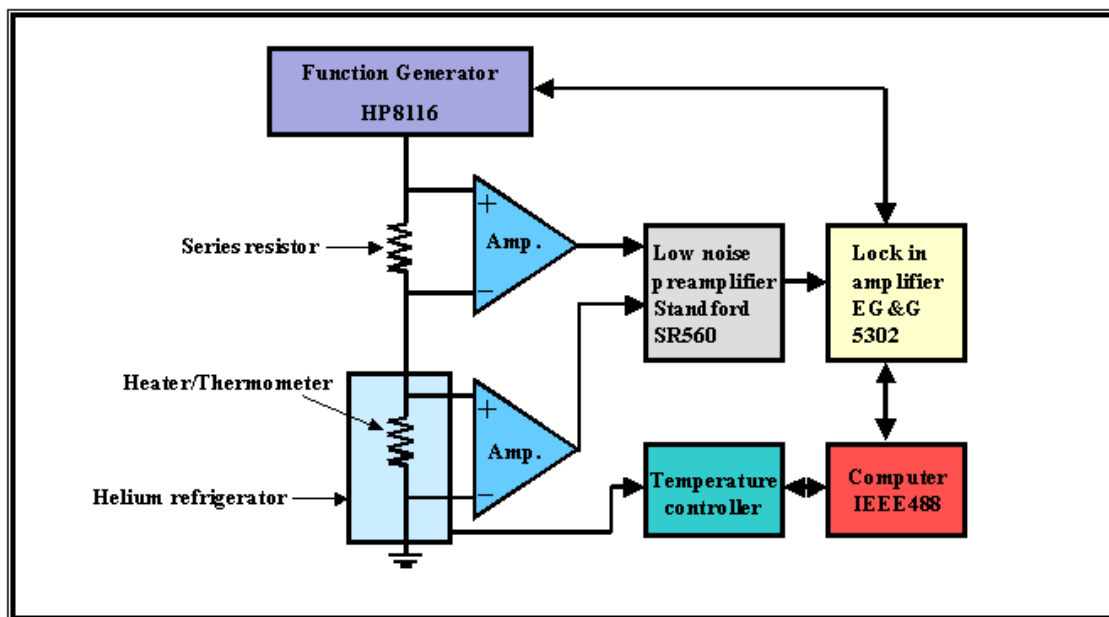


Fig. 2 The schematic diagram of the 3ω thermal conductivity apparatus.

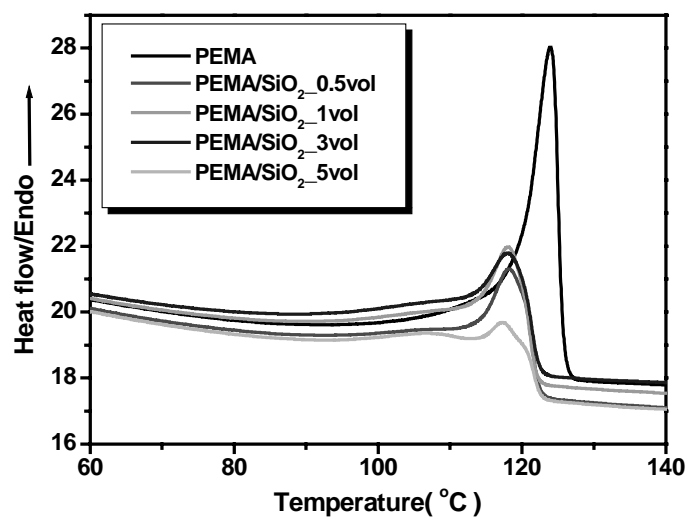


Fig.3 The melting behavior thermogram of the PEMA/SiO₂ composites.

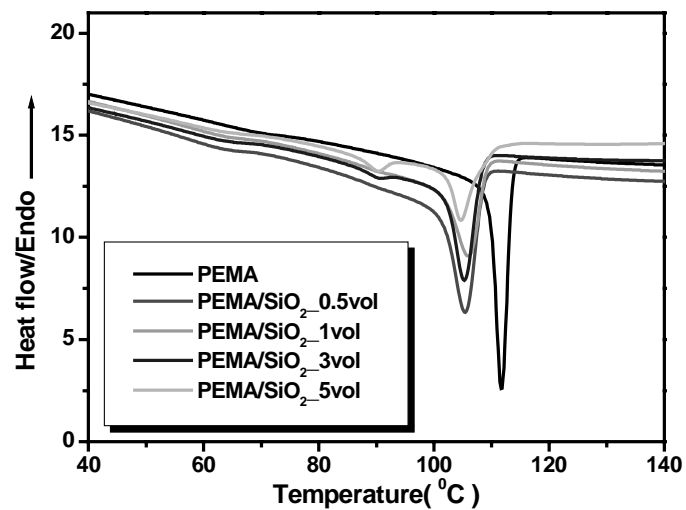


Fig.4 The crystallization behavior thermogram of the PEMA/SiO₂ composites.

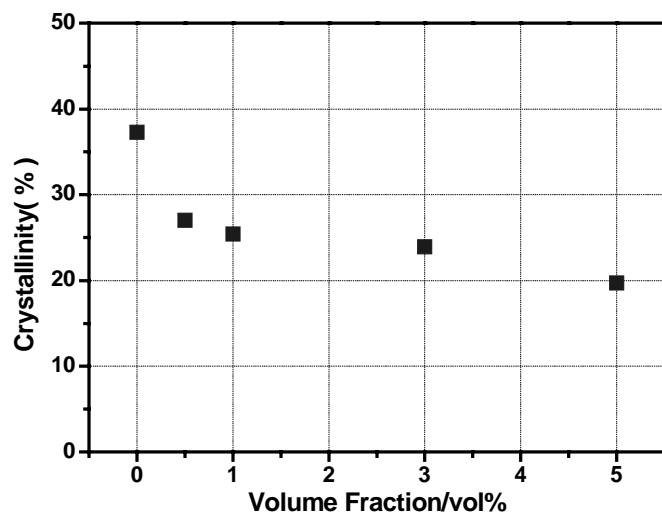


Fig. 5 The crystallinity of the PEMA/SiO₂ composites.

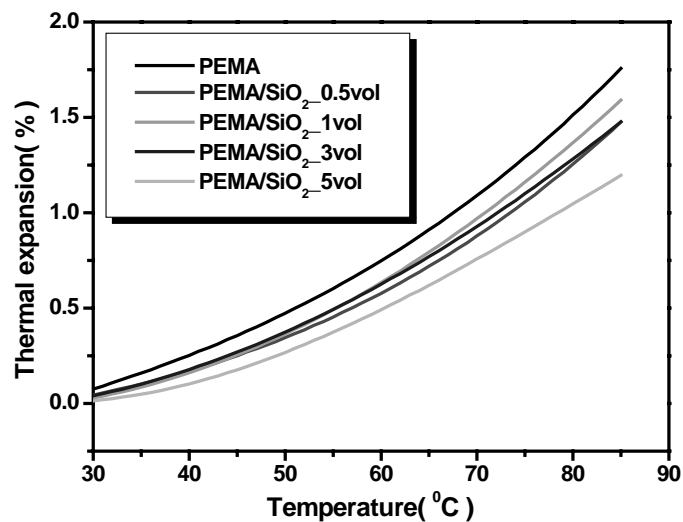


Fig. 6 Thermal expansion of the PEMA/SiO₂ composites.

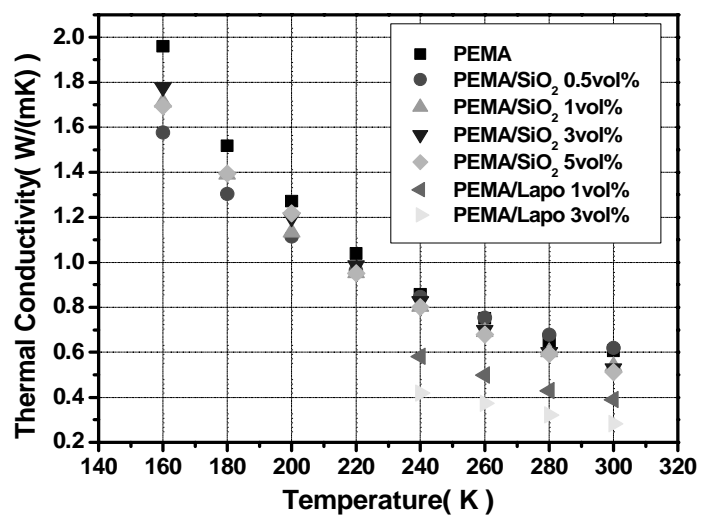


Fig.7 Thermal conductivity of the PEMA/SiO₂ and PEMA/Lapo nanocomposites.

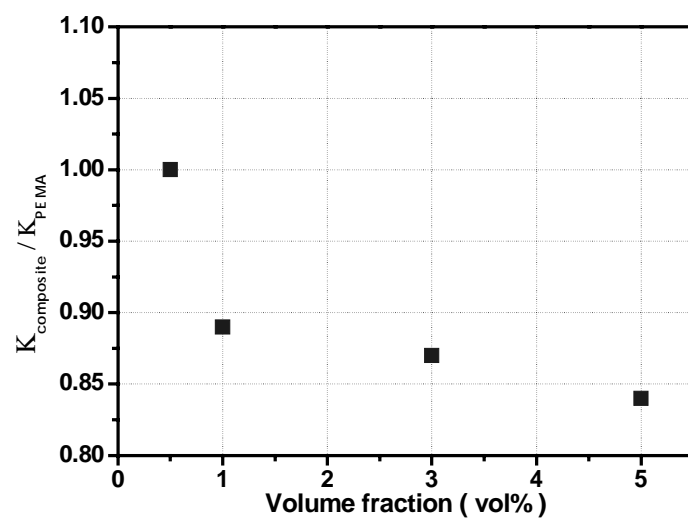


Fig.8 Thermal conductivity vs. volume fraction of SiO_2 .